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Temperature Variation of the Zero-Field Splitting in $CdCl_2 : Mn^{2+}$

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The expressions derived previously for the zero-field splitting in trigonal symmetry have been used here to study the temperature dependence of the splitting in $CdCl_2 : Mn^{2+}$ in the temperature range 20–710°K. It has been assumed that a strictly external point-charge point-multipole model is valid. If one considers, because of the lack of available data on the temperature variation of the lattice parameters, that the *c* dimension of the hexagonal unit cell of the crystal increases linearly with temperature, it is possible to explain the splitting at temperatures below 300 °K. To interpret the splitting in the entire range of temperature meaningfully, the structure parameters at these temperatures must be known rather accurately.

I. INTRODUCTION

In a previous paper[1] the zero-field splitting of a ^6S ion in a trigonal symmetry has been studied theoretically based on a point-multipole model. The expressions for the splitting under different mechanisms involving spin-spin and spin-orbit interactions and crystal fields were analyzed in details. It was shown that both the spin-spin and spin-orbit interactions were important. The present paper is a theoretical attempt to understand the temperature dependence of the splitting in $CdCl_2 : Mn^{2+}$ as observed experimentally by Hoeve and Van Ostenburg.[2]

In Sec. II, the expressions derived in Ref. 1 for various mechanisms are used for estimating the splitting parameter D in $CdCl_2 : Mn^{2+}$ at temperatures (in °K) – 20, 96, 300, 510, 620, and 710 for which the experimental results are available. Crystal structure data corresponding to these temperatures (except at room temperature) have not yet been reported for $CdCl_2$. However, the unpublished results for the crystal structure data at 300 and 600 °K by Hoeve and Van Ostenburg are available and found useful for our analysis. These data show that the *a* dimension of the hexagonal unit cell of $CdCl_2$ remains constant, whereas the *c* dimension increases very much with temperature. The average value of the coefficient of linear expansion of the crystal along the *c* axis is estimated from these data. Further, assuming that the coefficient of linear expansion remains constant with temperature we obtain the *c* dimension of the cell at the required temperatures. Using these values, the splitting at different temperatures are calculated and compared with experiments. Sec. III is devoted to the conclusion.

II. RESULTS AND DISCUSSION

In order to estimate the splitting from various mechanisms in $CdCl_2 : Mn^{2+}$, one is required to know the crystal fields B_2^0 and $(B_4^0)'$ (see Ref. 1 for the notations) at the magnetic ion. The crystal structure parameters for $CdCl_2$ have been given by Pauling and Hoard[3] at room temperature and are listed in Table I where a_H and c_H denote, respectively, the *a* and *c* dimensions of the hexagonal unit cell of the crystal. The only other available data are at 300 and 600 °K as obtained by Hoeve and Van Ostenburg[4] by analyzing the x-ray diffraction pattern at these temperatures (see Table I). Table I shows that the data by Pauling and Hoard at room temperature agree closely with the corresponding data obtained by Hoeve and Van Ostenburg. It must also be noted that the experimental errors in the latter data are not known. A comparison of the structural data at 300 and and 600 °K makes clear that the parameter c_H undergoes a large change (of about 2.5%) as one goes from 300 to 600 °K, whereas the parameter a_H remains constant. It is therefore reasonable (though it is not strictly valid) to assume for our analysis that the *a* dimension of the unit cell does not alter throughout the range of temperature under consideration. As for the parameter c_H one may determine it by assuming that the coefficient of linear expansion remains independent of temperature. Though this assumption is not quite correct, it is justified in the absence of crystal structure parameters at other temperatures. We are now confronted with the problem of evaluating the crystal fields B_2^0 and $(B_4^0)'$. However, the parameter *u* (see Table I) will also be involved for their calculations through the coordinates of the atoms. From Table I one knows that *u* is uncertain by the amount ± 0.01 according to the measurements of Pauling and Hoard. On the other hand, Hoeve and Ostenburg's data give *u* near to 0.25 at both 300 and 600 °K if it is assumed that the experimental error in their data is very small. The exact value of *u* is

TABLE I. Crystal structure parameters of $CdCl_2$.

Reference	T (°K)	a_H (in Å)	c_H (in Å)	u	Positions of Cd^{2+} ion	Positions of Cl^- ions
Pauling and Hoard[a]	300	3.85	17.46	0.25 ± 0.01	$(0, 0, 0)$	$(0, 0, u)$, $(0, 0, \overline{u})$
Hoeve and Van Ostenburg[b]	300	3.851	17.450	0.25	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{3})$	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{3}+u)$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{3}-u)$
	600	3.851	17.870	0.25	$(\frac{2}{3}, \frac{1}{3}, \frac{2}{3})$	$(\frac{2}{3}, \frac{1}{3}, \frac{2}{3}+u)$, $(\frac{2}{3}, \frac{1}{3}, \frac{2}{3}-u)$

[a] See Ref. 3. [b] See Ref. 4.

of particular concern to us since the zero-field splitting parameter D is found to be very sensitive[1] to the value of u; it changes from -2×10^{-4} cm^{-1} to $+11\times10^{-4}$ cm^{-1} at room temperature as one goes from $u = 0.24$ to 0.26 to cover the uncertainty in u. This is easy to understand if one notes that the distance of a Cl^- ion in the crystal measured from magnetic ion depends on the product uc_H (see Table I). Since c_H is a large number, a slight variation in u changes the relevant distances by a large amount and produces a large change in D. In the present analysis, since the experimental errors in the parameter u as given by Hoeve and Van Ostenburg are not known, it is reasonable to assume $u = 0.25$ throughout the range of temperature.

The calculated results for B_2^0, $(B_4^0)_{nc}$, $(B_4^3)_{nc}$, and $(B_4^0)'$ (see Ref. 1) at different temperatures are tabulated in Table II which corresponds to $u = 0.25$ and c_H/a_H as determined by the above method. Next D_{BO-1}, D_{BO-2}, D_{ODS}, D_{WC}, and D_{SS} are calculated following the method of Ref. 1. These are shown in Table III. In Table IV the total contribution to D has been listed and compared with experiment at various temperatures. The experimental result at 20 °K has been obtained by Hall *et al.*[5] As for the results at 300 °K, there are two values available. One, which gives $D < 5\times10^{-4}$ cm^{-1}, is obtained from the experiments of Koga *et al.*[6] The other value equal to 1×10^{-4} cm^{-1} is deduced from Fig. 2 of Ref. 1 which displays the experimental D value of Hoeve and Van Ostenburg as a function of temperature. This figure was drawn simply to show that the uncertain value $< +3\times10^{-4}$ cm^{-1} of Ref. 2 could be replaced by a more exact value, 1×10^{-4} cm^{-1}. In Table IV (for the sake of comparison), we have also listed the total theoretical contributions to D for different temperatures corresponding to $u = 0.2445$ which is chosen such that the value of D lies close to the experiment, namely, 1×10^{-4} at 300 °K.

If one compares the theoretical results at different temperatures for $u = 0.25$ with the corresponding experimental results in Table IV, one concludes that the experimental results can be explained reasonably well at temperatures below 300 °K. At higher temperatures, however, the theoretical results deviate considerably from experiment. One of the reasons for this discrepancy may lie in using the approximate values of the lattice structure parameters c_H and keeping u and a_H constant with temperature. The calculated results for $u = 0.2445$ in Table IV show that D can be changed by large amounts simply by changing the parameter u slightly. Thus, the structure parameters must be known with better precision.

Since we have not estimated the contributions to D from overlap and charge-transfer covalency effects, one is inclined to believe that the inclusion of these effects may explain the splitting in the entire range of temperature. However, we show below that these effects are not dominant (but may be significant and should not be ignored). It must be emphasized that our point-charge contributions depend on a large number of ions in the lattice and, as seen above, are close to the experimental results below 300 °K. The overlap and charge-transfer covalency contributions, on the other hand, mainly depend on the ligand ions which, in our case, form a regular octahedron[2] at temperature, say T_0 (which is close to 300 °K), consequently giving zero contribution to D. The overlap and charge-transfer covalency contribution at some temperature above T_0 will be nearly equal and

TABLE II. Crystal-field parameters B_2^0, $(B_4^0)_{nc}$, $(B_4^3)_{nc}$, and $(B_4^0)'$ at different temperatures for $u = 0.25$. The fields B_2^0 and $(B_4^0)'$ are in units of $10^{-2}e^2/2a_0^3$ and $10^{-4}e^2/2a_0^5$, respectively; the $(B_4^0)_{nc}$ and $(B_4^3)_{nc}$ are in units of $10^{-2}e^2/2a_0^5$.

T (°K)	c_H/a_H	B_2^0	$(B_4^0)_{nc}$	$(B_4^3)_{nc}$	$(B_4^0)'$
20	4.4295	−1.929	0.1733	0.1783	2.416
96	4.4571	−1.973	0.1736	0.1764	2.604
300	4.5313	−2.093	0.1743	0.1715	3.083
510	4.6076	−2.214	0.1746	0.1664	3.539
620	4.6476	−2.276	0.1746	0.1638	3.763
710	4.6803	−2.327	0.1746	0.1616	3.939

TABLE III. Parameter D in units of 10^{-4} cm^{-1} from various mechanisms at temperatures corresponding to the crystal fields in Table II.

T (°K)	$D_{BO\text{-}1}$	$D_{BO\text{-}2}$	D_{ODS}	D_{WC}	D_{SS}(total)
20	+8.10	−5.28	−4.09	−6.41	+14.09
96	+8.28	−5.69	−4.28	−6.71	+14.42
300	+8.79	−6.74	−4.81	−7.55	+15.29
510	+9.29	−7.74	−5.39	−8.44	+16.17
620	+9.55	−8.23	−5.69	−8.93	+16.63
710	+9.77	−8.61	−5.95	−9.33	+17.00

TABLE IV. Comparison of the calculated values of D for two cases corresponding to $u = 0.25$ and 0.2445 with the experimental results at different temperatures.

T (°K)	D(total) in units of 10^{-4} cm^{-1} $u = 0.25$	$u = 0.2445$	D(in units of 10^{-4} cm^{-1}) Experiment
20	+6.41	+2.84	$+\ 4.93 \pm 0.16$[a]
96	+6.02	+2.39	$+\ 3.67 \pm 0.33$
300	+4.98	+1.20	$\sim +1$[b] $< +5$[c]
510	+3.90	−0.003	$-\ 4.33 \pm 0.33$
620	+3.34	−0.63	$-\ 9.67 \pm 0.50$
710	+2.88	−1.14	-11.33 ± 0.33

[a] See also Ref. 5.
[b] From Fig. 3 of Ref. 1.
[c] See Ref. 6.

opposite to that when the temperature is below T_0 by the same amount. [This is clear if one considers that the ligand ions lie on planes above and below the plane containing the magnetic ion and that the planes move apart as the temperature increases. In other words, the octahedron becomes elongated along the z axis if the temperature is increased above T_0 and becomes compressed if the temperature is decreased below T_0. For the detailed discussion the reader is referred to Ref. 2. This situation should be compared with a different octahedral environment (see Refs. 2 and 3 cited in Ref. 1), where the expressions for the overlap and charge-transfer effects are derived, to understand the change in D with the distortion of the octahedron.] Now, because the point-charge results below 300 °K are close to the experimental results it can be concluded that the overlap and charge-transfer contributions are not dominant below 300 °K (if one wants to maintain agreement with experiment). If this is the case then the overlap and charge-transfer contributions above 300 °K (which will be nearly equal and opposite in sign) are also expected to be small. Thus, we infer that such contributions will not be dominant in our system. However, only the detailed calculations can prove the validity of this statement. Such calculations, besides being tedious and expensive in terms of machine computation, are meaningful only when the crystal structure parameters are known accurately since, as we have seen above, the splitting is very sensitive to the structure parameters, especially u.

III. CONCLUSION

We have made an attempt to understand the temperature dependence of the zero-field splitting in $CdCl_2 : Mn^{2+}$ based on the point-charge point-multipole model. It has been shown that the splitting parameter D can be explained reasonably well below 300 °K if one assumes a constant value (determined from the available data on the crystal structure parameters) of the coefficient of linear expansion. The overlap and charge-transfer contributions are concluded not to be dominant. The splitting is sensitive to the changes in the structure parameters and, therefore, the structure parameters should be known accurately at different temperatures before the theory can be compared reasonably with experiment.

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